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## 19. ABSTRACT

The reactions are discussed in terms of transition state theory, with tunneling where appropriate. Potential alternate reaction mechanisms and the combustion conditions under which they could occur are considered.

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## STATEMENT OF THE PROBLEM AND APPROACH

Knowledge of the kinetics of reactions taking place during propellant burning is essential to the development of improved energetic materials. Models lacking such information are devoid of physical significance and are of little use in extrapolation from one system to another. In the present work an HTP (high-temperature photochemistry) reactor has been used to measure the kinetics of a number of individual reactions, identified as important in propellant combustion models.

The high-temperature photochemistry (HTP) technique employed is uniquely useful to provide data over wider temperature ranges of interest than accessible by other techniques in use for making measurements on isolated propellant reactions. However, we found a photochemical approach unsuited for the study of one important class of reactants: nitroalkanes. In the final study we therefore modified the reactor to allow operation in a discharge-flow resonance-fluorescence mode. In this manner the reaction between H atoms and nitromethane was studied at higher temperatures than had been accessible to previous workers.

## RESULTS AND PUBLICATIONS

The majority of the results can best be summarized by the titles and abstracts of the resulting publications:

1. Paul Marshall and Arthur Fontijn, "A High-Temperature Photochemistry Study of the  $D + ND_3$  Reaction", *The Journal of Physical Chemistry*, 91, 6297 (1987).

The kinetics of the  $D + ND_3$  reaction (2) has been studied from 590 to 1220 K by using the high-temperature photochemistry (HTP) technique.  $D(^1S)$  atoms were generated by flash photolysis of  $NH_3$  and monitored by time-resolved atomic resonance fluorescence with pulse counting.  $k_2(T)$  is determined to be  $3.2 \times 10^{-10} \exp(-8810 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Accuracy assessments are discussed in the text. Comparison to  $k_1(T)$  for  $H + NH_3$  (1) measured in the same apparatus and over a similar temperature range shows that  $k_2(T)$  is smaller.  $k_1(T)$  and  $k_2(T)$  agree reasonably well with calculations based on transition-state theory and a simple tunneling model using the same potential energy surface for both reactions. Considered alone,  $k_2(T)$  can also be modeled with tunneling.

2. Paul Marshall, Taeho Ko, and Arthur Fontijn, "High-Temperature Photochemistry Kinetics Studies of the Reactions of H(<sup>1</sup>S) and D(<sup>1</sup>S) with N<sub>2</sub>O", The Journal of Physical Chemistry, 93, 1922 (1989).

The H + N<sub>2</sub>O(1) and D + N<sub>2</sub>O(2) reactions have been investigated by using the high-temperature photochemistry (HTP) technique. Empirical fits to the pressure-independent rate coefficients yield  $k_1(T) = 4.2 \times 10^{-14} \exp(-2290 \text{ K}/T) + 3.7 \times 10^{-10} \exp(-8430 \text{ K}/T)$  and  $k_2(T) = 3.5 \times 10^{-13} \exp(-3600 \text{ K}/T) + 5.3 \times 10^{-10} \exp(-9170 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the ranges 410-1230 and 450-1210 K, respectively. The 2 $\sigma$  precision of these results is better than 11% and the 95% accuracy limits are assessed at about  $\pm 25\%$ . The kinetic isotope effect  $x(T) = k_1(T)/k_2(T)$  decreases from 2.2 at 450 K to 1.3 at 1200 K, behavior contrary to classical transition-state theory which predicts  $x(T)$  increasing with temperature. The data are qualitatively consistent with a rate-controlling step that is dominated by tunneling at the lower end of the temperature range.

3. Taeho Ko, Paul Marshall, and Arthur Fontijn, "Rate Coefficients for the H + NH<sub>3</sub> Reaction over a Wide Temperature Range", The Journal of Physical Chemistry, 94, 1401 (1990).

The temperature dependence of the rate coefficients for the H + NH<sub>3</sub> → NH<sub>2</sub> + H<sub>2</sub> reaction is measured by the high-temperature photochemistry (HTP) technique. Technique improvements are discussed. For the 490-960 K range, we find  $k_1(T) = 1.21 \times 10^{-10} \exp(-6920 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . When combined with two other sets of direct measurements, a best fit gives  $k_1(T) = 9.0 \times 10^{-19} (T/\text{K})^{2.40} \exp(-4991 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the 490-1780 K range. It is shown that these data can be more closely fitted by a calculation based on conventional transition-state theory plus an Eckart tunneling model than with other current transition-state models considered. Using the potential energy surface for the H + NH<sub>3</sub> reaction, several tunneling models fit the results for the D + ND<sub>3</sub> reaction. The kinetic isotope effect for these two reactions is compared to results from different theoretical models, with the Eckart model giving the best approximation.

4. Taeho Ko and Arthur Fontijn, "A High-Temperature Photochemistry Kinetics Study of the Reaction H + NO<sub>2</sub> → OH + NO from 296 to 760 K", The Journal of Physical Chemistry, in press.

Rate coefficients for the H + NO<sub>2</sub> → OH + NO reaction have been measured using the high-temperature photochemistry (HTP) technique. H atoms are generated by flash-photolysis of CH<sub>4</sub> and their relative concentration is monitored by time-resolved resonance-fluorescence. The data are well-fitted by the empirical expression  $k(T) = 2.2 \times 10^{-10} \exp(-182 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the 296-760 K temperature range. The precision of the data is 7% and the accuracy is estimated to be 21%, where both figures represent 2 $\sigma$  statistical confidence intervals. Comparison of the ratio of the experimental reaction cross sections, at the temperature extremes, to the theoretical ratio supports a zero energy barrier. The potential stabilization channel leading to HONO is discussed.

5. Taeho Ko and Arthur Fontijn, "A Flow Tube Kinetics Study between Ground-State Hydrogen Atoms and Nitromethane", The Journal of Physical Chemistry, to be submitted.

The kinetics of the  $\text{H} + \text{CH}_3\text{NO}_2$  reaction have been studied using the discharge flow-resonance fluorescence (DF-RF) technique. H atoms are produced from microwave discharges through  $\text{NH}_3/\text{Ar}$  mixtures. The data in the 360-570 K range are well fitted by the empirical expression  $k(T) = 1.0 \times 10^{-11} \exp(-1981 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Precision of the data is better than +11% and the accuracy is estimated to be about  $\pm 20\%$ , where both figures represent  $2\sigma$  statistical confidence intervals. Results of some experiments where  $\text{H}_2$  was discharged indicate that the channel leading to OH and  $\text{CH}_3\text{NO}$  is significant for the title reaction.

Preliminary work has been done on the  $\text{K} + \text{O}_2 + \text{M}$  muzzle flash reaction using our newly developed Metals-HTP technique, first used for the  $\text{Na} + \text{O}_2 + \text{M}$  reaction [see, P. Marshall, A.S. Narayan and A. Fontijn, J. Phys. Chem., 94, 2998 (1990)]. In this work K atoms were produced by flash lamp or 193 or 248 nm excimer laser photolysis of KI or KCl. Using a hollow cathode lamp, too weak a signal was obtained to meaningfully measure K-atom kinetics. However, recent work in our laboratory has shown that the increased sensitivity of laser-induced fluorescence allows the making of measurements in the Metals-HTP reactor, where hollow-cathode lamp induced signals are too weak. Thus the study of this reaction in future work remains possible, if a suitable dye laser dedicated to this type of investigation can be obtained.

With the completion of the work reported here, the unique significance of HTP reactors to elucidation of O/N/H system kinetics is well established. However, to extend the work, reactions of radical species such as NH and  $\text{NH}_2$  would be the most important to address. Such experiments (like K-atom observations) required a dye laser system to monitor these radicals by their fluorescence. (For the O- and H-atom reactions of this report, self-built discharge-flow lamps were used to excite the fluorescence.) The laser, and associated detection electronics, would have to be in essentially full-time use in such studies. We are investigating the possibilities for obtaining this equipment, without which we are not currently recommending a continuation of our type of work.

## **LIST OF PARTICIPATING SCIENTIFIC PERSONNEL**

Professor Arthur Fontijn, Principal Investigator

Dr. Paul Marshall, Postdoctoral Fellow

Taeho Ko, Graduate Student

A.S. Narayan, Graduate Student

William F. Flaherty, Group Technician

Mr. Ko received a masters degree by his successful defense of a candidacy proposal, based on the work described above. It is anticipated that he will receive the Ph.D. degree within the year, which will again be largely based on ARO-supported work.

## **CONTACTS WITH ARMY LABORATORY PERSONNEL**

Throughout the course of this work we have had extensive contacts with BRL Scientific Personnel, particularly Drs. W.R. Anderson and A.W. Miziolek. We regularly visited BRL, Dr. Anderson visited here and further interactions took place at various meetings on the chemistry of energetic materials. Major discussion topics were: (i) the selection of reactions for our work to fit into BRL models and interest, and (ii) construction of a modified HTP reactor for BRL experiments to supplement the Rensselaer work.